

The Use of C-Near Edge X-Ray Absorption Fine Structure Spectroscopy for the Elaboration of Chemistry in Lignocellulosics

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ABSTRACT

The research presented elucidates the oxidation chemistry occurring in hydrogen peroxide bleached kraft pulp fibers by employing carbon near edge x-ray absorption fine structure spectroscopy (C-NEXAFS). C-NEXAFS is a soft x-ray technique that selectively interrogates atomic moieties using photoelectrons (X-rays) of variable energies. The X1A beam line at the National Synchrotron Light Source (NSLS) was employed to probe carboxylic acid groups that display a signature absorption band at 289 eV. This study is the capstone to a larger effort to support the mechanistic basis for lignocellulosic fiber chemical degradation induced by the disproportionation of hydrogen peroxide during fiber bleaching. We present X-ray absorption spectra obtained using a scanning transmission X-ray microscope (STXM) at the end of a 2.5 GeV electron synchrotron that provided $1s \rightarrow \pi^*$ contrast-enhanced micrographs illustrating random distributions of carboxylic acids that were principally located on fiber surfaces. Control studies using non bleached fibers demonstrated that very little signature carboxylic acid absorption patterns were present in the fibers suggesting that these groups are a fingerprint for macroscopic fiber strength damage during non radical suppressed hydrogen peroxide bleaching.

INTRODUCTION

The use of hydrogen peroxide for the bleaching of kraft pulp fibers represents a new paradigm for the production of environmentally compatible, low opacity paper. Hydrogen peroxide is a powerful oxidant whose oxidizing ability has been used in many industries, including bleached pulp production, cotton scrubbing and bleaching, and wastewater remediation (1-3). Complete capture of its oxidation potential is difficult since several of its disproportionation pathways favor the production of nonselective radicals such as hydroxide. Since pulp fibers are mainly comprised of carbohydrate chains having glucose monomer repeat units up to 10^6 , any radical activity has the potential to induce β -elimination reactions resulting in chain cleavage that arise from anomeric carbon oxidation. The Fenton-type cycle can induce cellulosic damage as a result of glycosidic cleavage reactions which are observed as attenuations in fiber tensile strength (4).

Although these cleavage reactions result in diminished macroscopic properties, no work until this point has provided a rational assessment of the chemical pathways at the molecular level that lead to the observed compromised physical properties. One of the main issues in determining chemically-induced damage at the microscopic level is the tremendous heterogeneity in the chemical composition of the pulp. Pulp is composed of an array of biomaterials such as lignin, cellulose, and hemicelluloses. Traditional methods of visualization like AFM, SEM, and TEM do not provide a detailed understanding of the chemical damage that is induced in pulp through hydrogen peroxide disproportionation reactions. Recently it was determined that TOF-SIMS, however, can provide a remarkable topographical distribution of metal ions on lignocellulosics that is functionally dependent on bleaching and the ensuing chemistry (5). Nevertheless, this method still suffers from an inability to probe chemical functional groups in a manner similar to NMR. Obtaining chemical composition at high spatial resolution is a requisite for determining the chemistry occurring during hydrogen peroxide bleaching of pulp that leads to physical strength losses. Although such a measurement is challenging, high chemical specificity and resolution are possible using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

The high spatial resolution provided by X-ray microscopy has the potential to characterize the chemical changes occurring at the molecular level in pulp, a feat that has heretofore never been accomplished at the high level of accuracy and precision available to this technique. It is important to decipher the basis for the chemical changes in pulp, since these lignocellulosic samples are known to exhibit stress in their compositional integrity as a result of the oxidation reactions that occur during bleaching. For example, the intrinsic viscometry of the carbohydrate components of pulp is reduced during extended bleaching conditions resulting from the cleavage and peeling reactions (6). Yet, there have been no clear correlations of the changes occurring at the molecular level with the macro level observables. Our initial efforts in the study of hydrogen peroxide-induced pulp damage suggested that carboxylic acid moieties are the chemical markers pursuant to the radical activity. We fortuitously discovered that the metal distribution of select metals (iron, manganese, magnesium) was systematically redistributed on a pulp surface following bleaching by using TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry), a surface analytical technique. They were distributed in concentrated aggregates or clusters in a manner suggesting the possibility of a severely oxidized site characterized by a preponderance of carboxylic acid functionalities. In fact, we had ESCA and NMR data that suggested a strong accretion of these groups, but were unable to definitively identify them.

In this study, we intend to focus on the chemical sensitivity and utility of the carbonyl core ($C\ 1s, O\ 1s \rightarrow \pi^*_{C=O}$) transitions to probe the thesis of this work. The $C\ 1s$ and $O\ 1s$ NEXAFS spectra of a control and hydrogen peroxide bleached pulp sample are presented. C -NEXAFS has been used in the past to probe the

electronic structure of organic carbon within microheterogeneous samples similar to ours to provide very conclusive functional group information (7, 8). The present work describes our efforts to clearly establish the localization of carboxylic acid functionalities in a distribution and topology that is concurrent with their development as a result of the oxidative damage process incurred by pulp fibers from hydrogen peroxide bleaching.

EXPERIMENTAL

Preparation of Substrates. All samples used were obtained from a Northern black spruce tree approximately 30 year of age that was sectioned according to age (juvenile wood – top 8 feet, mature wood, bottom trunk of tree), debarked, chipped, and stored. All pulp samples were prepared according to standard kraft pulping techniques by an industrial sponsor. The control sample (unbleached) was a typical mature hand sheet sample, whereas the bleached sample was bleached according to protocols described previously (9). The samples were cut into square sheets of approximately 2 cm x 2 cm size. The samples were then prepared for mounting a standard TEM gold grid surface using a modified epoxy resin embedding procedure. The following procedure was done to ensure proper epoxy-fiber embedding and penetration to avoid delamination effects during microtoming: the pulp samples were soaked piecemeal in water, ethanol (three times), and propylene oxide (three times) for 10 minutes each. Finally, they were soaked for curing in propylene oxide/Epon resin (1:1 w:w) followed by neat Epon for 1 hour each to ensure homogeneous distribution of Epon by propylene oxide. The sample was then placed under vacuum overnight to remove excess propylene oxide and sandwiched between polyethylene sheets. After curing of the Epon resin, the samples were precisely microtomed according to standard procedures, mounted onto TEM grids, and stored for transport to Brookhaven National Labs.

Carbon micro-NEXAFS Measurements. Carbon NEXAFS data were acquired using the scanning transmission X-ray microscope (STXFM) and microspectrometer located at the X1A beam line that are located at the National Synchrotron Light Source at Brookhaven National Laboratories in Upton, NY. The X-ray source is an undulator on the 2.5 GeV electron storage ring. The current configuration of the STXFM monochromator is capable of 0.3 eV energy resolution and a spatial resolution of approximately 40 nm. X-ray microfocusing is done by diffraction limited optics using a Fresnel phase-zone plate objective and an order sorting aperture (Jacobsen et al. 1991). In order to obtain microspectra, the monochromator must be in the scanning mode while the sample is simultaneously stepped along the z-axis to maintain focus (a stepper motor drive is used with drift up to 1 μ in the the x-y axes). The actual window for analysis is approximately 100 x 100 nm due to these positioning errors (10). The data collection were accomplished by acquiring an absorption spectrum spanning the energy range of 280-310 eV which was corrected for background noise/storage current drift by subtraction of a spectrum without the sample. The data are presented in the absorption mode as the $-\log (T/T_0)$, in which T and T_0

are the transmittance of the sample and the background, respectively. Typical spectra span a wavelength range of 3 Å and include 512 points with a dwell time of 100 ms. Energy calibration is provided by comparison of the position of the 1s- π^* transition with the Rydberg transitions of CO₂ that is bled into the irradiated volume (11)

RESULTS AND DISCUSSION

One of the first challenges in our early work was differentiating the signal that evolved from the embedding matrix versus the paper sample given the absorption maxima for aromatic residues at the near C edge. We found that clear contrast at 285 eV was possible for the hydrogen peroxide bleached black spruce fiber sections as shown in Figures 1a-d in which the fiber and the background can be distinguished.

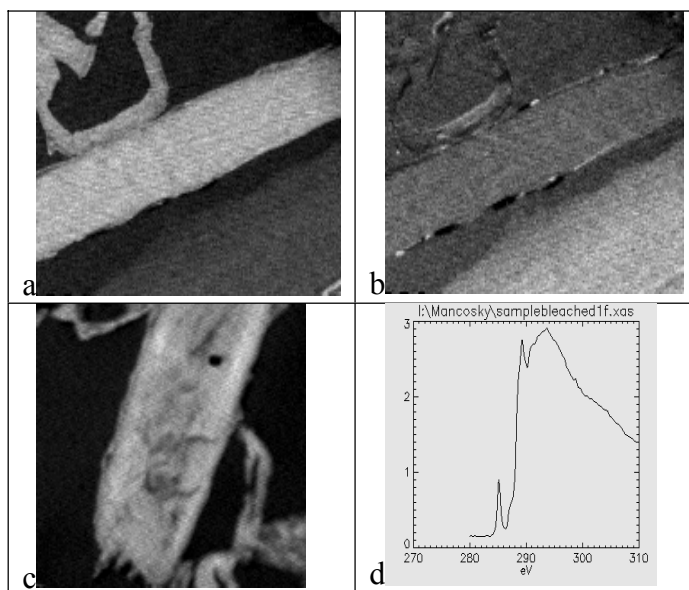


Figure 1. The above photomicrographs are illustrative of the following: **a)** unbleached fiber (white) in resin (gray) 72 μm across; **b)** the same photomicrograph as **a)** except with contrast adjusted to highlight pits; **c)** a bleached fiber section approximately 50 μm across; and **d)** represents a sample steady-state absorbance spectra of the fiber in **c)**.

Once differentiation of the matrix and sample components was established, we initiated a stacked spectral acquisition to compare and contrast the various regions in a $45\mu^2$ area. It was found from our analysis that there was a relatively pronounced spectrum after employing the 289 eV energy for visualization which we were able to correlate to the COOH 1s $\rightarrow \pi^*$ transition. Figure 2 demonstrates a representative spectral output at this energy.

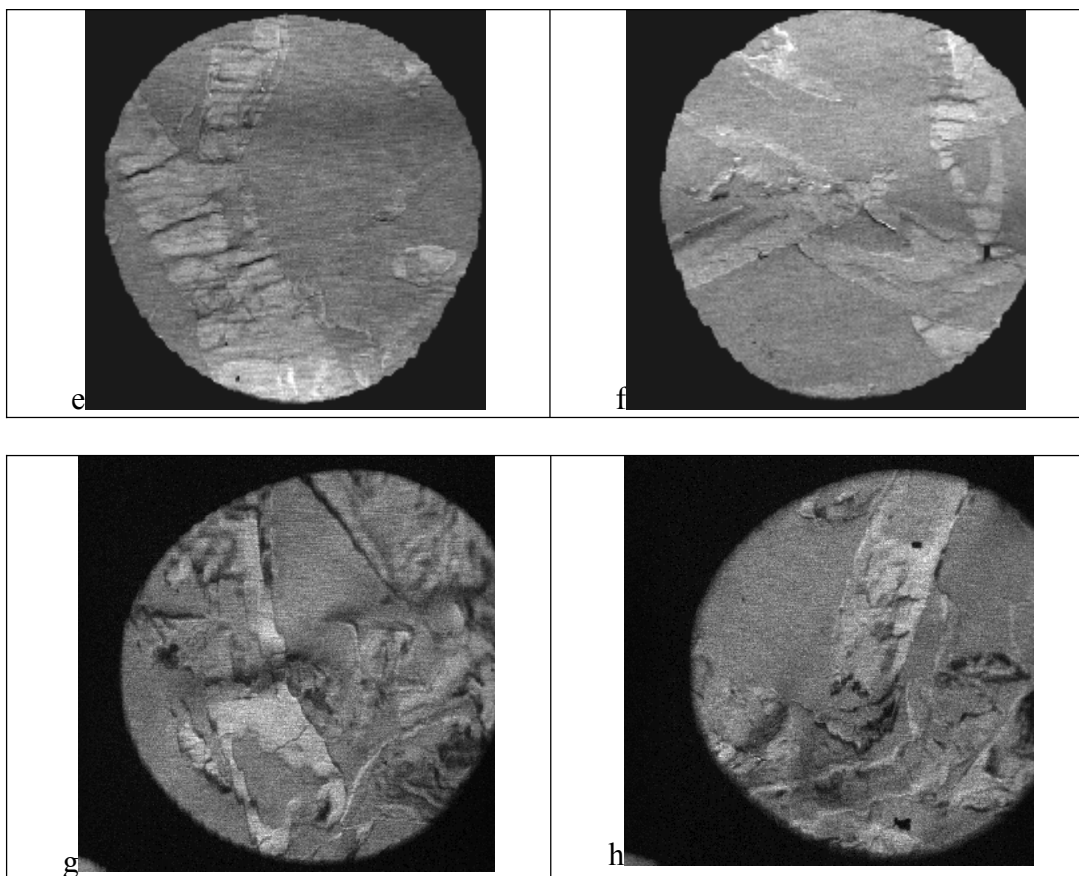


Figure 2. The above photomicrographs represent the following: **e)** unbleached fibers at 289 eV; **f)** unbleached fibers at 289 eV; **g)** bleached fibers at 289 eV; and **h)** bleached fibers at 289 eV. (All holes are approximately 125 μm across)

It is easy to observe the $\text{COOH } 1s \rightarrow \pi^*$ absorption that is localized along the edge of the fiber sections since it is depicted as a more intensely concentrated dark area. Interestingly, the spectral window for this transition was observed to be relatively narrow. STXM is a transmission technique and therefore dark bands are occasionally visible due to folds in the sample, effectively doubling the thickness and not allowing for the transmission of the x-ray energy at any wavelength. This was tested by sweeping multiple wavelengths and was found to not be the case for any of the carboxylic rich regions. Figure 3 demonstrates the spectral display for the same fiber using 0.5 eV increments on either side of 289 eV. It is obvious that 289 eV is indeed the maximum for the COOH transition. Although work done by Cody indicates that this transition is at lower energies (287.5 eV), it is well appreciated that the electronic environment plays a critical role in affecting C 1s transition energies. The analysis of the maturation of the vitrinite coals as studied by Cody provides an approximate value for the near edge transition that is clearly a function of its interaction with similar energy transitions.

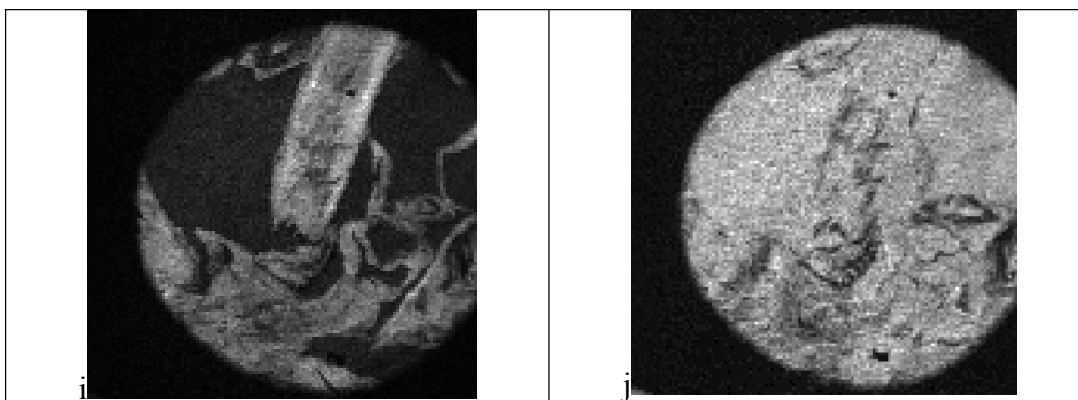


Figure 3. In **i**), the absorbance profile of bleached fibers at 288.5 eV is shown, whereas **j**) demonstrates the absorbance of bleached fibers at 289.5 eV. (All holes are approximately 125 μm across)

Our previous studies strongly suggested that the oxidation chemistry that is observed in the hydrogen peroxide bleaching of pulp fibers mainly occurs at the surface of the fiber.¹ We were able to develop a working theory through the data collected from potentiometric, TOF-SIMS, ESCA, and SEM measurements that indicated that the chemical differences contributing to fiber tensile strength degradation mainly arise from radical chemistry that gives rise to oxidation of the carbohydrates and lignin, ultimately providing carboxylic acid functionalities. In order to lend sufficient evidence to this theory, it was necessary to acquire a large sampling of fibers to observe the localized topographic occurrence of these acids that display a distinct spectral signature at 289 eV. As evidenced in the previous Figures, the bleached samples all display a degree of absorption at 289 eV that is mainly localized on the periphery of the substrate. This localization is consistent with a surface-mediated oxidation chemistry that arises from metal-catalyzed disproportionation of the hydrogen peroxide. Control studies in our labs as well as those of others indicate that this event can be mitigated by efficient removal of the metals through appropriate chelation measures (12). In fact, these topological signatures are consistent with the surface acid enrichment of hydrogen peroxide-bleached pulp data acquired in our labs. The striking absence of these motifs on the periphery of the control pulp fibers provides ample support for the proposal that acid accretion is a by-product of hydrogen peroxide-mediated pulp damage, mainly incurred in the carbohydrate moieties, specifically cellulose. The totality of our initial data suggested that the brunt of the damage sustained by kraft fibers was borne by the load-bearing portion or cellulose regions. Interestingly, supporting data in this lab has shown that oxygen-mediated bleaching schemes cause an enrichment of crystalline cellulose domains with a concomitant drop in the level of amorphous cellulose domains (13).

The current work represents the first concerted effort at establishing the nature of the fiber damage sites that occurs during the hydrogen peroxide bleaching of non-

¹ Work done under the auspices of an industrially funded consortium at the IPST Center at the Georgia Institute of Technology strongly suggested this chemistry.

chelated fibers. This technique is extremely powerful for the determination of organic functional groups with high specificity and without the issue of spectral noise arising from coupled transitions since the analytical method is essentially a quasi-atomic absorption technique.

CONCLUSIONS

The data provides the first x-ray interrogation of the chemical features of hydrogen peroxide bleached kraft softwood pulps that define the molecular origin of the damage that the fibers sustain during the bleaching process. The carboxylic acid moieties that absorb at 289 eV are abundant at the edges of the microtomed fibers, lending evidence to the postulation that hydrogen peroxide-induced fiber damage is a topochemical Fenton event. These metals have been authenticated by TOF-SIMS as well as ICP.

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